

MILD OXIDATIVE SOLUBILIZATION OF COAL MACERALS

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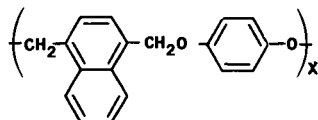
The objective of this study is to solubilize coal macerals and an Argonne Premium Coal Sample using oxidation and to characterize these soluble products. A major problem in coal characterization and in coal utilization is the intractability of the coal macromolecular network. High temperature treatments yield smaller, volatile and soluble molecules, which can be greatly altered from their original structures, along with a significant amount of a non-volatile char. Mild oxidation should provide a soluble mixture of compounds in higher yields and with structural characteristics more like the original coal. The approach described in this paper attempts to oxidatively cleave only activated benzylic sites in the coal macromolecules in a two step process. In the first step benzylic sites which are partially active due to oxygen functionality either on the aromatic ring or on the benzyl carbon are further activated by the formation of pyridinium salts at that carbon from the reaction with pyridine and iodine. In the second step this carbon is oxidized by alkaline silver oxide resulting in formation of carboxylic acid groups. This process has been described in an initial communication for whole coals (1) and the results of the first reaction on the macerals, used in this study, has been published (2). This report will focus on the yields of the oxidation step and the characterization of the products.

A few oxidative degradation studies on separated coal macerals have been published (3-5). In these studies there was extensive oxidation and only small molecules were identified. In this study, both smaller and higher molecular weight fractions which were separated on the basis of solubility have been characterized using gel permeation chromatography (GPC), GCMS, Pyrolysis MS (PyMS) the precise mass measurement mode, Fast Atom Bombardment (FAB) MS, and NMR. FAB MS has proven to be useful in the characterization of polar biological compounds. This is the first application of this technique to coal oxidation products. Since FAB is a relatively mild ionization technique, it should help to characterize products with molecular weights greater than 500. Compounds in this range are not volatile enough for GCMS and are broken down into smaller fragments by PyMS. However, the chance of rearrangements in PyMS are reduced when pyrolysing the oxidation products in comparison to the whole coals or maceral concentrates. It is interesting to note the remarkable lack of large polycyclic aromatics in the soluble products. The significance of this result will be discussed.

EXPERIMENTAL

Samples

A description of the macerals and whole coal is given in Table 1. Details of the maceral separation have been reported (2). The Upper Elkhorn and the Brazil Block samples have been separated from coals obtained from Pennsylvania State University labelled PSOC 1103 and PSOC 828, respectively. The subbituminous coal is the Argonne Premium Coal Sample (APCS) number 2, which has been recently mined and has been stored under nitrogen in sealed glass ampoules. The preparation of the oxy-methylene linked polymer(I) has been described (6).



(1)

Oxidations

The pyridinium salts of the samples were prepared by refluxing 1 g of the coal, maceral or polymer in 60 ml of pyridine with 4 g of iodine for 70 hrs (2). The reaction mixture was poured into 10% aqueous NaHSO_3 and the solution filtered. The derivatized coal was washed free of pyridine, dried and analyzed. In a typical oxidation fresh Ag_2O , prepared from 8.5 g of AgNO_3 and sodium hydroxide, was refluxed with 1.0 g of the substrate in 50 ml of 10% aqueous NaOH for 20 hrs. The silver and unoxidized samples were removed by filtration and the filtrate acidified with aqueous HCl . Products which were alkaline soluble but insoluble in the slightly acidic solution were termed humic acids. The solubles were extracted with $\text{Et}_2\text{O-MeOH}$. Yields were determined by analysing the products for carbon. The products were methylated with diazomethane for further analysis.

Characterization

Approximate molecular size distributions were determined by gel permeation chromatography using a set of three ultra-Styrigel columns with 100, 500, and 1000 Å nominal pore diameters. The samples were eluted with THF and detected by UV at 254 nm. The columns were calibrated using a set of esters of known molecular weight.

GCMS and PYMS data were obtained on a Kratos MS-25 mass spectrometer. A 60 m x 0.25 mm DB-1701 fused silica column was used in GCMS analysis. The details of the PYMS experiment have been reported (2). The samples were all heated at 50°/min on a platinum screen and the instrument was operated in the precise mass measurement mode. The FABMS data were obtained on a VG 70-250 at the University of Chicago, Chemistry Department. Argon gas was used with glycerol as the probe matrix. NMR data were taken on a Bruker AM-300 using CDCl_3 as a solvent.

RESULTS AND DISCUSSION

The yields for the oxidation step are very sample dependent as is shown in Table 1. The yields are calculated based on the carbon content of the starting material and of the products with the values given being an average of at least two experiments. The oxidation of the Illinois No. 2 vitrinite yielded 84% of the original carbon in the soluble products. This result can be contrasted with the fusinite where only 47% of the carbon has been recovered of which 40% was the $\text{Et}_2\text{O-MeOH}$ soluble fraction. If one assumes that fusinite is "fossil charcoal", then this result is expected. The number of pyridinium salts formed (1.5/100 carbons) is small and suggests that much of the oxygen occurs as heterocyclics. In addition, there were probably less benzylic carbons in this fusinite compared to the vitrinite. The lower yield for the sporinite, 62%, compared to the vitrinite may reflect

the greater aliphatic content of the sporinite which would be resistant to oxidation. The APCS #2 has a similar composition to the Illinois No. 2 vitrinite and yields essentially the same amount of solvent solubles but less humic acid material. Oxidation of the polymer gives only 1,4-naphthalenedicarboxylic acid. No evidence the naphthalene ring oxidation has been found. It is interesting to note that one naphthalene-dicarboxylic acid is formed for every pyridinium salt.

The Et₂O/MeOH soluble fraction does have a significant amount of higher molecular weight materials as is seen in the GPC data from the methyl esters presented in Figure 1. The molecular size scale is only approximate and this approach works best for comparisons. Figure 1a compares Illinois No. 2 vitrinite with fusinite. The fusinite gives a narrower distribution shifted to a larger molecular size compared to the vitrinite. A comparison of the solvent solubles and humic acid from Upper Elkhorn vitrinite is shown in Figure 1b. The humic fraction higher MW peak is significantly higher than the corresponding peak for solvent soluble. Since this is a fairly mild degradation the molecular size distribution is typically at a much higher MW compared to pyrolysis products of the sample samples. Finally, it is interesting to note the difference in Figure 1c of the output from a UV and a fluorescence detector which are in-line. The chromatograms have been normalized, but the poor signal-to-noise from the fluorescence detector is a good indication of the lack of fluorescing compounds such as polycyclic aromatics in the product.

Proton NMR data lends support to the observation of the lack of polycyclic aromatics. Since even the solvent soluble fractions contained compounds which are too large and non-volatile for GCMS, the proton NMR spectra have been taken. The methyl ester region is the most informative and is shown for the Illinois No. 2 samples in Figure 2. From the spectra of a number of known methyl esters, three regions can be assigned: 3.6-3.8 aliphatic, 3.8-4.0 single ring aromatics and heteroaromatics, and 4.0-4.2 polycyclic aromatics and heteroaromatics. Single-ring aromatics and aliphatics are the most abundant species in these samples.

Compounds that can be separated by GCMS are mostly benzene, and hydroxybenzene carboxylic acids. The total ion chromatogram for APCS #2 is shown in Figure 3. Although this is a fairly mild oxidant, tetra-, penta- and hexa carboxylic acids are still formed. Also note even the hydroxybenzene tetra- and penta-carboxylic acids are formed. More model compounds are being examined to better understand this result. In addition to benzene and hydroxybenzene carboxylic acids, furan carboxylic acids are found in significant abundance.

Fragments found by PyMS with APCS #2 and the vitrinites are dominated by aliphatics and single ring aromatics and hydroxylated aromatics. PyMS of the humic products results in volatilization at lower temperatures as compared with the coal or maceral, as is shown in Figure 4. Comparing the pyrolysis products between the two samples, the most striking difference is the reduction in aliphatics in the humic acid fraction. Figure 5 shows the distribution of hydrocarbons found as a function of Z-number (hydrogen deficiency, 0-alkane, 1-alkene, 4-benzene, etc.). However, in each case the contribution of fragments with more than 1 aromatic ring was small, 5.6% for the coal and 4.6% for the oxidation product. A milder ionization approach has been taken with some of these samples. A FAB MS spectrum for the solvent solubles from the Upper Elkhorn vitrinite is shown in Figure 6. Again, peaks which can be identified as single ring compounds dominate. However, unlike electron impact peaks are seen at M/Z > 400. The conditions for this experiment need to be optimized and a matrix more suitable than glycerol used. Also, some of these samples will be analysed using field ionization MS.

All of these results strongly suggest that for our vitrinite samples and the subbituminous coal sample the single ring aromatics dominate. Unlike many other experiments most of the carbon is characterized using this approach. More model compounds and polymers are being studied to verify the selectivity of this derivatization/oxidation procedure.

ACKNOWLEDGEMENTS

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TABLE 1. Coal and Maceral Samples.

Sample () [†]	Source	Rank	Empirical Formula	Py [†] /100°C	Ag ₂ O Oxidation Yields*	
					Organic Soluble %	Humic Acid %
APCS #2	Rawhide Seam	Subbituminous	C ₁₀₀ H ₈₇ N _{1.4} S _{0.4} O _{19.6}	4.1	~40	26
Vitrinite (95+)	Illinois #2	HvC Bituminous	C ₁₀₀ H ₈₇ N _{1.5} S _{0.8} O _{18.3}	3.8	44	40
Fusinite (95+)	Illinois #2	HvC Bituminous	C ₁₀₀ H ₆₄ N _{0.8} O _{1.1}	1.5	40	7
Vitrinite (93)	Upper Elkhorn	HvA Bituminous	C ₁₀₀ H ₈₃ N _{1.9} S _{0.5} O _{10.5}	4.6	---	---
Sporinite (91)	Brazil Block	HvA Bituminous	C ₁₀₀ H ₁₁₅ N _{1.2} S _{0.8} O _{10.7}	3.8	46	16
Polymer-I			C ₁₈ H ₁₄ O ₂	2.4		44 [†]

[†]Maceral petrographic composition.

*Based on carbon composition.

[†]Mole percent.

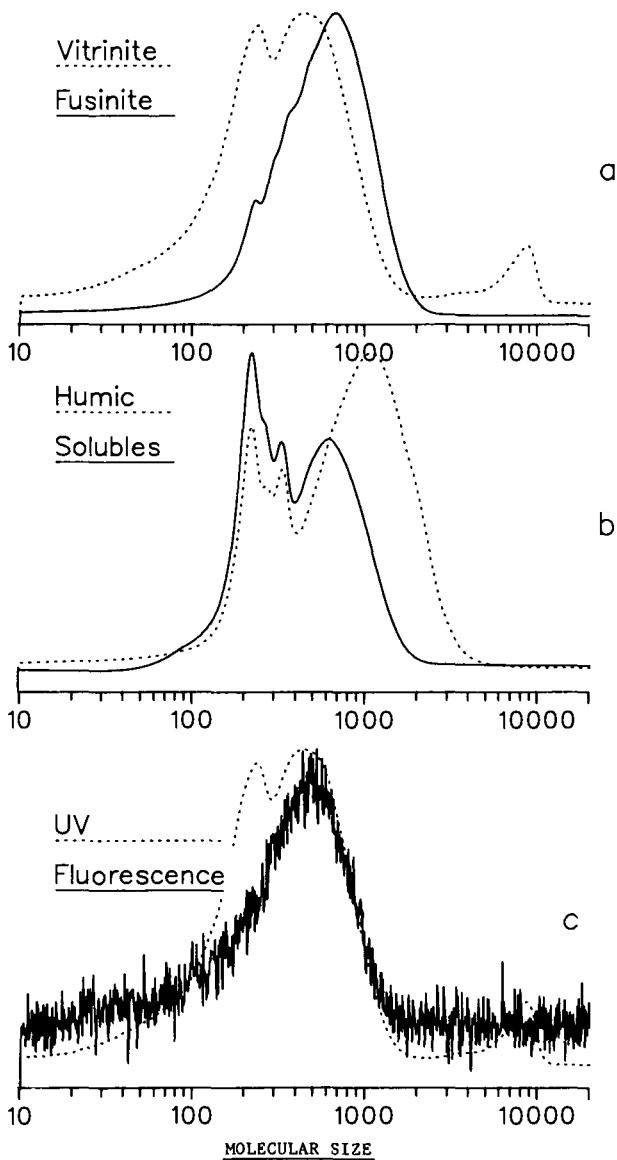


Figure 1. Gel permeation chromatograms of methyl esters: a) Illinois No. 2, solvent soluble fraction; b) Upper Elkhorn No. 3 vitronite, and c) Illinois No. 2 vitronite solvent soluble fraction.

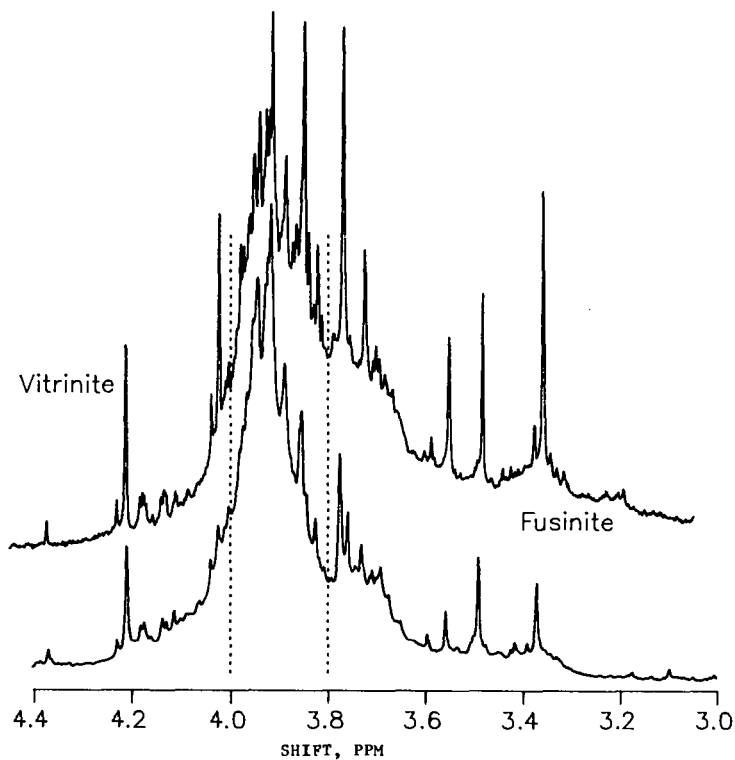


Figure 2. ^1H NMR spectra of Illinois No. 2 solvent soluble fraction, esters.

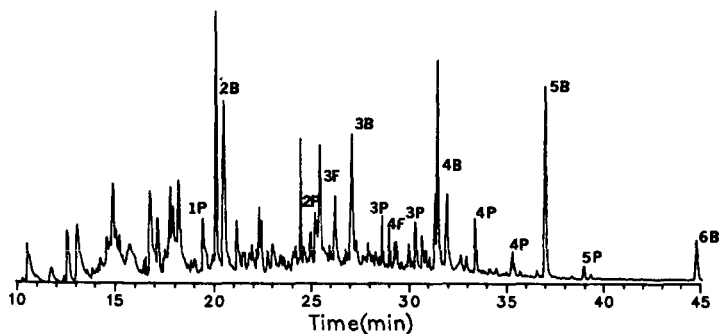


Figure 3. Total ion chromatogram of APCS #2 solvent soluble fraction, methyl esters. Major peaks: 2B-6B number of carboxylates on benzene, 2P-5P number on phenol and 2F-4F number of carboxylates on furans.

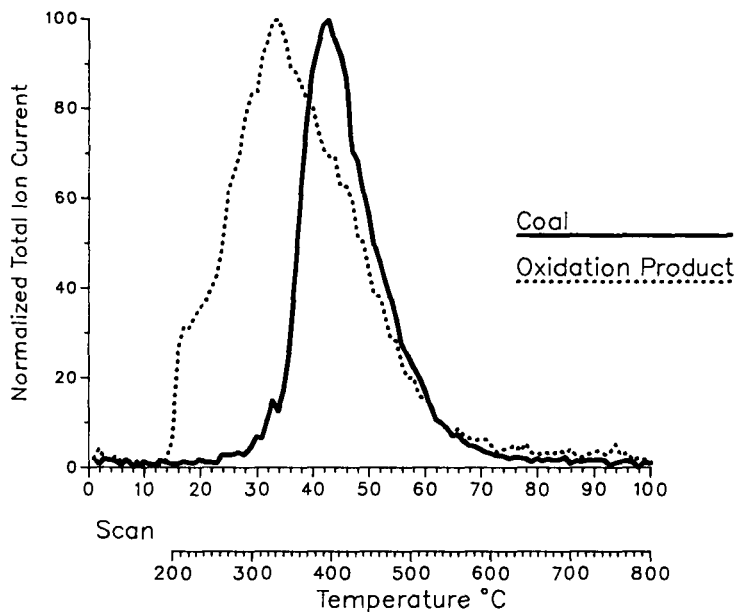


Figure 4. Total ion pyrograms for APCS #2.

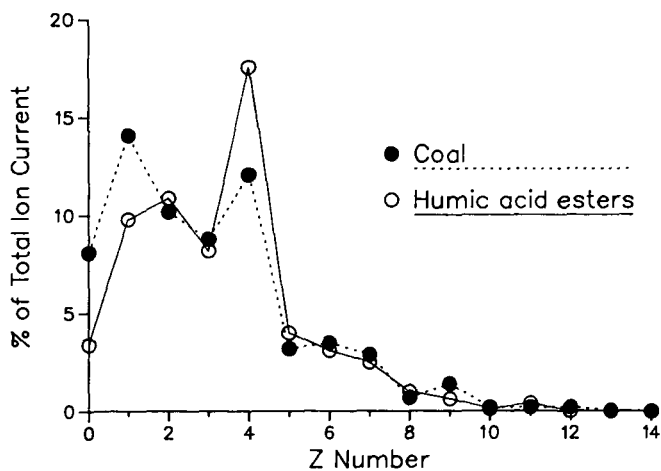


Figure 5. Distribution of hydrocarbons with Z-number for average of the data shown in Figure 4.

Figure 6. FAB mass spectra of Upper Elkhorn No. 3 vitrinite solvent soluble fraction, methyl esters.

